

PATENT COOPERATION TR. Y

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 16 March 2000 (16.03.00)	
International application No. PCT/IB99/01326	Applicant's or agent's file reference PCT/1999/011
International filing date (day/month/year) 27 July 1999 (27.07.99)	Priority date (day/month/year) 29 July 1998 (29.07.98)
Applicant VAN DYK, Jacobus, Philippus et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

14 February 2000 (14.02.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Juan Cruz
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

COMMUNICATION IN CASES FOR WHICH
NO OTHER FORM IS APPLICABLE

To:

LE ROUX, Marius
D.M. Kisch Inc.
P.O. Box 781218
2146 Sandton
AFRIQUE DU SUD

Date of mailing (day/month/year) 19 April 2001 (19.04.01)	
Applicant's or agent's file reference PCT/1999/011	REPLY DUE see paragraph 1 below
International application No. PCT/IB99/01326	International filing date (day/month/year) 27 July 1999 (27.07.99)
Applicant IPCOR N.V.	

1. ☐ REPLY DUE within _____ months/days from the above date of mailing
- ☐ NO REPLY DUE, however, see below
- ☒ IMPORTANT COMMUNICATION
- ☐ INFORMATION ONLY

2. COMMUNICATION:

It has been brought to the attention of the International Bureau (WO) that in respect of the above-identified application, the international publication No. WO00/01326 mailed on 10 february 2000 spelled WALPOLE, Ernest, Alan's name incorrectly.

The International Bureau shall publish a correction in Section II of the PCT Gazette. A corrected version of the pamphlet will be published on that same day.

A copy of this Notification has been sent to the receiving Office (RO/IB) and to the elected Offices concerned.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Maria Victoria CORTIELLO
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PCT/1999/011	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IB 99/ 01326	International filing date (day/month/year) 27/07/1999	(Earliest) Priority Date (day/month/year) 29/07/1998
Applicant IPCOR N.V. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

BENEFICIATION OF TITANIA SLAG BY OXIDATION AND REDUCTION TREATMENT

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

The abstract has to be changed as follows:
Line 1, after "relates" insert "to".

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 99/01326

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B34/12 C01G23/047

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 315 742 A (TIOMIN RESOURCES INC) 11 February 1998 (1998-02-11) the whole document	1-22
Y	WO 97 19199 A (QIT FER TITANE INC ;BOROWIEC KRZYSZTOF (CA); GRAU ALFONSO E (CA);) 29 May 1997 (1997-05-29) cited in the application	1-22
X	claims 1-38; examples 1-17	23
Y	US 3 739 061 A (STICKNEY W ET AL) 12 June 1973 (1973-06-12) column 3, line 31 - line 43; example 1	1-7
A	US 5 389 355 A (GUEGUIN MICHEL) 14 February 1995 (1995-02-14) column 4, line 60 -column 6, line 42	1-9, 11-16
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 October 1999

Date of mailing of the international search report

14/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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Authorized officer

Bombeke, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 99/01326

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 176 159 A (DE MENDONCA PAULO AYRES FALCAO ET AL) 27 November 1979 (1979-11-27) claims 1-4; examples 1,2 ---	4,5,17, 19,20
A	GB 1 282 506 A (BRITISH TITAN LIMITED) 19 July 1972 (1972-07-19) claims 1-4 -----	1-13,19, 20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 99/01326

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 2315742	A	11-02-1998	CA	2182123 A	27-01-1998
			AU	6438396 A	05-02-1998
			NO	965190 A	27-01-1998
			NZ	299283 A	19-12-1997
			US	5885324 A	23-03-1999

WO 9719199	A	29-05-1997	US	5830420 A	03-11-1998
			AU	7558896 A	11-06-1997
			CA	2210743 A	29-05-1997
			NO	980106 A	20-05-1998

US 3739061	A	12-06-1973	NONE		

US 5389355	A	14-02-1995	CA	1329006 A	03-05-1994
			NO	180803 B	24-03-1997

US 4176159	A	27-11-1979	NONE		

GB 1282506	A	19-07-1972	CA	930554 A	24-07-1973
			CA	927611 A	05-06-1973
			DE	2038191 A	11-02-1971
			DE	2038247 A	04-03-1971
			FR	2053367 A	16-04-1971
			FR	2053370 A	16-04-1971
			US	3649243 A	14-03-1972
			ZA	7005320 A	29-03-1972

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference PCT/1999/011	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IB99/01326	International filing date (day/month/year) 27/07/1999	Priority date (day/month/year) 29/07/1998
International Patent Classification (IPC) or national classification and IPC C22B34/12		
Applicant IPCOR N.V. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
 - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 14/02/2000	Date of completion of this report 23. 08. 2000
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Bombeke, M Telephone No. +31 70 340 3576 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/IB99/01326

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-27 as originally filed

Claims, No.:

1-19 with telefax of 27/07/2000

Drawings, sheets:

1/3-3/3 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IB99/01326

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-18
	No:	Claims	19
Inventive step (IS)	Yes:	Claims	1-18
	No:	Claims	19
Industrial applicability (IA)	Yes:	Claims	1-19
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The document WO-A-9719199 is regarded as being the closest prior art to the subject-matter of independent process claims 1 and 6, and insofar as this claim can be understood (see Section VIII), this document shows the all the features thereof with the exception that the oxidizing treatment is carried out at a temperature of above about 950°C, preferably from 1000°C to 1100°C.

The subject-matter of claims 1 and 6 therefore differs from this known process in that the oxidizing treatment is performed in less harsh conditions at a temperature of from about 700°C and above but below about 950°C such that an anatase phase is allowed to stabilize in the titania slag and the iron present in the slag is allowed to concentrate at the exposed slag particles.

The improvements obtained by the claimed novel process over WO-A-9719199 consist in the fact that titania slags wherein an anatase phase stabilizes during oxidation can be oxidized at lower temperatures and excellent upgrading to more than 90% TiO₂ can still be achieved even with atmospheric pressure leaching, which may give rise to major cost savings. No hint is found in the prior art as to the suitability of lower oxidizing temperatures for improving the beneficiation ability of titania slags containing pseudo-brookite as major phase and glassy phases of impurity oxides.

It follows that the subject-matter of claims 1-18 meets the criteria of Articles 33(2), 33(3) and 33(4) PCT in respect of novelty, inventive step and industrial applicability.

For independent product-by-process claim 19: see section VIII.

Re Item VIII

Certain observations on the international application

Claims 1 and 6 do not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-matter in terms of the result to be achieved ("allowing an anatase phase to stabilize ..., allowing the iron to concentrate ...") which merely amounts to a statement of the underlying problem. The "additional" technical features necessary for achieving this result should have been added, e.g. the base composition of the titania slag and the oxygen concentration of the oxidizing atmosphere.

Moreover the use of the vague term "about" is unsuitable to delimit the claimed oxidizing temperature range (upper limit) in an unambiguously clear manner over the process of WO-A-9719199, which teaches a similar temperature as lower limit and also gives rise to migration of the iron present in the slag to the slag/grain boundaries.

In this connection the unclarity of the independent product-by-process claim 19, which does not comprise any particular product feature, is enhanced by the above obscurities to such an extent that the subject-matter of claim 19 not solely is indefinite (Article 6 PCT) but is apparently even not novel (Article 33(2) PCT) by being not clearly distinguishable from titania slags treated according to the process of WO-A-9719199.

CLAIMS

1. A method of treating titania slag to increase the leachability of impurities from the slag comprising the steps of
 - sizing the titania slag to a particle size from 75 to 850 μm ;
 - 5 • oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
 - 10 • reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state.
2. A method of treating titania slag to increase the leachability of impurities from the slag comprising the steps of
 - 15 • sizing the titania slag to a particle size from 75 to 850 μm ;
 - oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700 °C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to

convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and

- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes, to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state.

3. The method of either one of claims 1 or 2 wherein the iron present in the slag concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilise in the slag when the slag is oxidised.

4. The method of any one of the preceding claims wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.

5. The method of claim 4 wherein the oxidation is carried out at a temperature from about 800°C to about 875°C.

6. The method of any one of the preceding claims wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

7. The method of any one of the preceding claims wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

8. A method of beneficiating titania slag to increase the TiO₂ content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 µm;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

9. A method of beneficiating titania slag to increase the TiO₂ content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 µm;

- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes, allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a substantial portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

10. The method of either one of claims 8 or 9 wherein the leaching is conducted under pressure in excess of atmospheric pressure.

11. The method of either one of claims 8 or 9 wherein the leaching is conducted at atmospheric pressure.

12. The method of any one of claims 8 to 11 wherein the acid used in the leaching step is heated.

13. The method of any one of claims 8 to 12 wherein the acid used in the leaching step comprises hydrochloric acid.

14. The method of any one of claims 8 to 13 which includes a caustic leaching step after the acid leaching step.

15. The method of any one of claims 8 to 14 which includes a step of calcining the treated slag.

16. The method of claim 15 wherein the treated slag is washed and dried to remove volatile by products prior to the calcining step.

17. The method of either one of claims 15 or 16 wherein the calcined slag is subjected to a magnetic separation procedure.

18. The method of any one of claims 8 to 17 wherein the iron present in the slag concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilise in the slag when the slag is oxidised.

19. The method of any one of claims 8 to 18 wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.

20. The method of claim 19 wherein the oxidation is carried out at a temperature from about
5 800°C to about 875°C.

21. The method of any one of claims 8 to 20 wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

10 22. The method of any one of claims 8 to 21 wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

23. A product when formed by a method of any one of the preceding claims.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C22B 34/12, C01G 23/047	A1	(11) International Publication Number: WO 00/06786 (43) International Publication Date: 10 February 2000 (10.02.00)
(21) International Application Number: PCT/IB99/01326 (22) International Filing Date: 27 July 1999 (27.07.99) (30) Priority Data: 98/6758 29 July 1998 (29.07.98) ZA (71) Applicant (for all designated States except US): IPCOR N.V. [NL/NL]; Maduro Plaza, 19 Dok Road, Curacao (AN). (72) Inventors; and (75) Inventors/Applicants (for US only): <u>VAN DYK</u> , Jacobus, Philippus [ZA/ZA]; 585 Gerhard Marais Street, Constantia Park, 0010 Pretoria (ZA). <u>VEGTER</u> , Nanne, Mattheus [ZA/ZA]; 796 Thomas Avenue, Arcadia, 0083 Pretoria (ZA). <u>VISSER</u> , Cornelia, Petronella [ZA/ZA]; 4 Daniel Road, Pierre van Ryneveld, Centurion, 0157 Pretoria (ZA). <u>DE LANGE</u> , Thomas [ZA/ZA]; 18 Conglomerate Street, Zwartkop, Extension 8, Centurion, 0157 Pretoria (ZA). <u>WINTER</u> , John, David [AU/AU]; 3 Virgo Street, Elmore Vale, NSW 2287 (AU). <u>WALPONE</u> , Ernest, Alan [AU/AU]; 28 Chilcott Street, Lambton, NSW 2299 (AU). <u>NELL</u> , Johannes [ZA/ZA]; 49 Duiker Avenue, Randpark Ridge, Extension 22, 2156 Randburg (ZA).		(74) Agent: LE ROUX, Marius; D.M. Kisch Inc., P.O. Box 781218, 2146 Sandton (ZA). (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: BENEFICIATION OF TITANIA SLAG BY OXIDATION AND REDUCTION TREATMENT		
(57) Abstract <p>This invention relates to a method of treating titania slag to increase the leachability of impurities from the slag comprising the steps of sizing the titania slag to a particle size from 75 to 850 μm; oxidising the sized slag particles at a temperature from about 700 °C and above but below about 950 °C allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles and/or allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and reducing the oxidised slag in a reducing atmosphere from about 700 °C to about 950 °C to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state. The invention also relates to a method of beneficiating titania slag to increase the TiO₂ content thereof wherein the above treated slag is leached with acid.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
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BENEFICATION OF TITANIA SLAG BY OXIDATION AND REDUCTION TREATMENT

1. Field of the Invention

This invention relates to a method of beneficiating titania slag to a high grade titanium dioxide (TiO_2) product. Preferably the product is suitable for use as a feedstock in titanium
5 dioxide pigment production or titanium metal production by means of the chloride process. The invention also relates to a process for preparing intermediate products suitable for use in the beneficiation of titania slag and also to intermediate products and final products formed by the processes.

More particularly the process of the present invention includes the steps of sizing the slag;
10 oxidising the sized slag and then reducing the oxidised slag. The treated slag may then be subjected to steps such as acid leaching.

2. Background of the Invention

Commercial uses of TiO_2

Titanium is widely known for its use as a metal, but the primary use of titanium is in the form
15 of titanium dioxide (TiO_2). TiO_2 is used as a white pigment in paints, plastics and paper. Two types of pigment with a tetragonal crystal structure are produced, namely rutile and anatase. Rutile is preferred in outdoor paints and anatase is preferred in indoor paints.

TiO₂ pigment production

There are two commercial processes for the production of TiO₂ pigment namely, the sulphate process and the chloride process. A sulphate process plant is easier to operate and monitor than a chloride process plant, and is capable of using feedstock with a relatively low TiO₂ content. However, capital costs of a modern sulphate process plant can be higher than that of a chloride process plant of the same pigment capacity. Furthermore there is a higher volume of waste products to be treated and disposed of due to the use of more impure feedstock and the fact that the sulphate used in the process cannot be easily recovered and recycled.

Accordingly the chloride process is a more popular process and is growing in popularity. The feedstock suitable for use in the chloride process usually need to have a high TiO₂ content and need to contain fewer impurities than those suitable for the sulphate process.

TiO₂ bearing deposits

TiO₂ is commonly found in nature in the form of ilmenite (FeO. TiO₂) which contains from 40% to 80% TiO₂. Most deposits being mined produce concentrates with a TiO₂ content between 45% and 67%. Rutile deposits are far more scarce than ilmenite and they contain about 95% TiO₂ in crystalline form and are therefore of sufficient quality to be used directly in the chloride process for TiO₂ pigment production. Deposits of anatase have been discovered but have not yet been commercially exploited. Anatase typically has a TiO₂ content in excess of 95%. Leucoxene, a weathered form of ilmenite, contains up to 85% TiO₂ and is exploited on a limited commercial scale. Brookite (rhombic TiO₂), perovskite, (CaTiO₂), sphene (CaTiSiO₅) and geikielite (MgTiO₃) also contain titanium.

Beneficiation of ilmenite

Although natural rutile is suitable for use as a feedstock in the chloride process, the ever-decreasing availability of natural rutile forced chloride process pigment producers to consider other lower grade feedstock. One such alternative is naturally occurring ilmenite. Due to its relatively low TiO_2 content several processes have as their aim the upgrading of the TiO_2 content of ilmenite.

These processes include:

- i) Partial reduction of the iron in the ilmenite.

This process is described in US patents 4,038,364 and 4,199,552. In this process ilmenite is reduced at elevated temperatures to convert iron in the ferric state, (Fe(III)), to the ferrous state, (Fe(II)). This renders the iron more amenable to acid leaching of the ilmenite during upgrading of the ilmenite.

- ii) Pre-oxidation followed by partial reduction of the iron in the ilmenite.

In a process described in GB1,225,826 the ilmenite is subjected to an oxidation treatment to convert substantially all the iron to the ferric state. The ore is then reduced to convert the iron back to the ferrous state and metallic state. In the examples of the patent the oxidation is carried out at 870°C for two hours. The reduction is carried out at 870°C for five minutes. The ore exhibits the original X-ray diffraction pattern of ilmenite after treatment but is more amenable to acid leaching to upgrade the ilmenite.

- iii) Pre - oxidation followed by reduction of the iron to metallic state.

US patent 4,097,574 describes a process whereby ilmenite is subjected to an oxidation treatment to convert the iron in the ilmenite to the ferric state. Reduction treatment is then carried out to reduce the iron to metallic iron. The iron is then removed by leaching thereby to upgrade the ilmenite.

- iv) Smelting of the ore.

Ilmenite ore can also be smelted in the presence of a carbonaceous reducing agent in an electric arc furnace. This process is described in US patent 2,680,681. Two saleable products result from this namely, high quality pig iron and titania rich slag.

The slag typically contains 80 - 85% TiO_2 .

Differences between ilmenite ore and titania slag

All of the processes listed above are aimed at beneficiating ilmenite or similar titanium ores. None of these processes were applied to titania slag and there are certain fundamental differences between ilmenite ore and titania slag.

- i) The first difference is that ilmenite is a naturally occurring titanium bearing ore, while titania slag is produced by electro-smelting of ilmenite in an electric arc furnace.
- ii) The second difference can be found in the amount of the main components that are present. Ilmenite typically contains around 50% titanium oxide and around 45% iron oxide. All the titanium is present as Ti(IV) while around 20% of the iron occurs as Fe(III) and the rest is in the Fe(II) state. Titania slag typically contains around 85%

titanium oxide and around 10% iron oxide. In this instance the titanium is in the Ti(III) and the Ti(IV) state, while most of the iron is present as Fe(II).

iii) The third difference lies in the respective mineralogical compositions. In ilmenite concentrates the iron and the titanium is organised into hexagonal ilmenite crystals.

As-cast titania slag consists of the following four phases:

- a) The most abundant phase is a crystalline phase, known as pseudobrookite or the M_3O_5 phase. This phase is a solid solution of iron oxide and titanium oxide, with the end members being $(Ti,Fe,Al,Cr,V)_2O_3 \cdot TiO_2$ and $(Mg,Mn,Fe)O \cdot 2TiO_2$ and can accommodate the main oxidation states of iron and titanium in its structure, namely Fe(II), Fe(III), Ti(III) and Ti(IV);
- b) Rutile (TiO_2) although not always present in such quantities that allows detection thereof by X-ray diffraction analysis;
- c) An amorphous, glassy phase consisting mainly of SiO_2 , TiO_2 , FeO , CaO and Al_2O_3 and;
- d) Finely disseminated metallic iron globules present in the grain boundaries of the rutile crystals and in the silicate-rich glassy matrix.

The pseudobrookite and amorphous glassy phases are characteristic of titania slag and generally do not occur in ilmenite ores. The presence of pseudobrookite and the glassy phases in titania slag may be one of the causes that the processes for beneficiating ilmenite ore are in some cases not applicable to the beneficiation of titania slag. The different compositions of slags may also play a role.

Beneficiation of titania slag

Several known processes have as their aim the upgrading of the TiO_2 content of titania slag.

These processes can be classified as follows:

i) Chlorination of the impurities

5 A process is described in US patents 4,629,607; 4,933,153; 5,063,032 and 5,384,355 to upgrade titania slag containing at least one alkaline earth impurity. Firstly the slag is preheated in a fluidised bed reactor in an atmosphere void of oxygen to prevent the oxidation of the Ti(III) present in the slag to Ti(IV) . The slag is then contacted with hydrogen chloride gas. This results in the formation of iron and alkaline earth
10 chlorides in the slag. Finally the chlorides that formed during the chlorination treatment are leached with either water or hydrochloric acid.

ii) Salt roasting

In US patent 4,038,363 a process for the upgrading of slag is described. The process consists of a roast procedure in the presence of an alkaline salt such as sodium
15 chloride. After the roast procedure the agglomerates that have formed are dispersed with wet grinding. Thereafter the slag is subjected to leaching in either water or a sulphuric acid solution.

iii) Fluxing of the impurities

20 Titania slag can also be upgraded by heating the slag in the presence of a glass forming fluxing agent such as phosphorus pentoxide as is described in US patent 3,996,332. According to South African patent 93/5922 other glass forming agents such as the oxides of sodium, potassium, silicon etc. can also be used. After the

fluxing procedure the slag consists of a crystalline rutile phase and a glassy phase that contains most of the impurities present in the slag. Finally the slag is subjected to leaching in a mineral acid to remove the glass phase and associated impurities.

iv) Sulphatising

5 US patent 4,362,557 describes a process where the TiO_2 content of titania slag is increased in a two stage procedure. Firstly the slag is mixed with an alkaline salt such as sodium carbonate and reacted with either SO_3 or mixtures of SO_2 and O_2 at 700 to 1100°C. Secondly the sulphates that formed during the roasting are leached with either water or hydrochloric acid at room temperature.

10 v) Oxidation-reduction roasting

The process described in patent application PCT/CA96/00767 has as its basis an oxidation roast followed by a reduction roast. The slag is first sized in the range 75-850 μm and is then oxidised at a temperature of at least about 950°C, but preferably between 1000 and 1100°C, for at least 20 minutes. The oxidation procedure converts
15 the Fe(II) and Ti(III) present in the slag to Fe(III) and Ti(IV) respectively and aims to decompose the glassy phase. After the oxidation the slag is reduced at a temperature of at least about 700°C, but preferably between 800 and 850°C, for at least 30 minutes, but preferably for a period of 1,5 to 2 hours, to convert the Fe(III) in the slag back to Fe(II). A MgO rich ilmenite-geikielite solid solution forms during the
20 process, which is more amenable to leaching than the original phases present in the slag. The roasted titania slag is then leached under pressure in excess of atmospheric pressure and at a temperature of at least 125°C to remove the impurities present in the slag.

Patent application PCT/CA96/00767 referred to in the above paragraph also stresses the differences between the treatment of ilmenite and titania slag. In example 12 the application illustrates that the process of GB1,225,826 relating to the treatment of ilmenite (as discussed above) is not suitable when applied to titania slag. As in the case of the process of PCT/CA96/00767, the process of GB1,225,826 includes an oxidation and subsequent reduction treatment. However, negligible removal of impurities are achieved when the process of GB1,225,826 is applied to slag, that is by oxidising the slag with air at 850°C for 2 hours and then reducing it with smelter gas at 850°C for 5 minutes and thereafter leaching the resulting product with a hydrochloric acid solution under reflux conditions. Even if the process is modified by carrying out the oxidation at 900°C for 1 hour and the reduction at 900°C for 30 minutes (as set out in example 13 of PCT/CA96/00767) very poor results are achieved.

Patent application PCT/CA96/00767 teaches that the titania slag requires a pre-treatment within an unexpected window of process conditions to render it suitable for acid leaching. The patent describes much harsher oxidation, reduction and acid leaching steps for slag than the conditions for ilmenite as disclosed in the related process of GB1,225,826.

Most surprising it has now been found that if titania slag is oxidised at a lower temperature than that described in patent application PCT/CA96/00767 under the correct conditions and thereafter reduced and further treated, the slag can be suitably upgraded. In some embodiments of the invention it is not necessary to carry out the leaching at above atmospheric pressure. Leaching at a pressure above atmospheric pressure is required in the process of PCT/CA96/00767. It will be appreciated that

even if leaching at above atmospheric pressure may not be necessary for the successful beneficiation of titania slag according to the invention, the process will also function if acid leaching is carried out at above atmospheric pressure.

Patent application PCT/CA96/00767 teaches that during that process the iron cations tend to concentrate around pores formed in the slag particles which will render them more accessible to leaching. It is believed that if the oxidation step is carried out at lower temperatures as disclosed for the present invention the iron in the slag particles surprisingly migrates to the rims of the slag particles. It is believed that such slag particles undergo rapid reduction roasting and that such slag particles are more amenable to acid leaching which allows leaching to be conducted at atmospheric pressure.

3. Summary of the Invention

According to the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II)

state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state.

According to another aspect of the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- 5 • sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700 °C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted
10 to the Ti(IV) state; and
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes, to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state.
- 15 The titania slag includes a pseudobrookite phase and a glassy phase. The glassy phase may consist mainly of SiO_2 , TiO_2 , FeO and Al_2O_3 .

The titania slag may contain titanium oxide and impurities including at least one compound selected from the group consisting of iron oxide, silicon oxide, aluminium oxide, alkaline earth oxide, manganese oxide, chromium oxide and vanadium oxide. The titanium oxide and
20 impurities may be provided in a pseudobrookite phase and a glassy phase. The alkaline earth oxide may comprise calcium oxide and/or magnesium oxide.

The titania slag is preferably crushed and preferably to a particle range of above 106 μm up to 850 μm .

During the oxidation step the iron present in the slag preferably concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilise in the slag.

- 5 The oxidation is preferably carried out at a temperature from about 750°C and above but preferably below about 900°C and more preferably it is carried out at a temperature from about 800°C to about 875°C.

The oxidation is carried out for longer than 30 minutes. Preferably it is carried out for a period of about 2 hours.

- 10 The oxidation is preferably carried out in a fluidised bed reactor.

The oxidising atmosphere may comprise oxygen diluted by an inert gas (preferably a mixture of CO_2 and N_2) containing at least 2% oxygen by volume. More preferably the atmosphere results from the combustion of a carbonaceous fuel with excess air. Most preferably the oxidising atmosphere contains between 4% and 8% oxygen by volume.

- 15 Preferably more than 60%, preferably more than 75%, more preferably more than 90% and most preferably substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag. The reduction is preferably carried out at a temperature between about 800°C and about 875°C.

The reduction is preferably carried out in a fluidised bed reactor.

- 20 The reducing atmosphere may be supplied by any one of the following reducing agents: carbon monoxide gas, hydrogen gas, gases such as reformed natural gas and smelter off gas

and mixtures between these gases. More preferably the reducing atmosphere is supplied by the products resulting from combustion of coal.

The reduction is preferably carried out for a period of longer than 10 minutes and less than 1 hour. More preferably it is carried out for a period of 20 minutes.

5

Preferably more than 60%, preferably more than 75%, more preferably more than 90% and most preferably substantially all iron in the Fe(III) state is converted to the Fe(II) state during reduction.

Preferably less than 90%, more preferably less than 95% and most preferably none of the
10 titanium in the Ti(IV) state is converted to the Ti(III) state during reduction.

According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO_2 content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about
15 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for
20 at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II)

state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and

- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

5 According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO₂ content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 µm;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes, allowing an anatase
10 phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II)
15 state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

The leaching may be conducted under pressure in excess of atmospheric pressure.

20 Alternatively the leaching may be conducted at atmospheric pressure. Alternatively, a combination of atmospheric and pressure leaching may be used.

The acid may be heated and preferably the acid is heated to the boiling point of the acid.

The acid may comprise a mineral acid and preferably it comprises sulphuric acid or hydrochloric acid, more preferably hydrochloric acid.

5 The acid may be present in at least a 10% stoichiometric excess of what is needed to convert leachable oxides and alkaline impurities to soluble chlorides.

The acid leaching may be done in one or more stages. If more than one stage is used then the leaching may be done in co-current or counter-current mode.

The leaching may be done in batch or continuous mode.

10 The method of beneficiating titania slag may optionally include a caustic leaching step after the acid leaching step.

Optionally the method includes calcination of the treated slag. Prior to calcining the treated slag it may be washed and it may be dried to remove volatile by-products. The drying step may be carried out at a temperature above 100°C.

15 The calcination may be carried out by heating the product between 600°C and 900°C for more than 30 minutes.

The method may also include an additional step of subjecting the calcined slag to a magnetic separation procedure.

20 The methods of beneficiating the titania slag is preferably performed to form beneficiated titania slag suitable for use as a feedstock for the chloride process of TiO_2 pigment production.

The beneficiated titania slag may contain at least 90% by weight, preferably at least 94% by weight of titanium dioxide. Preferably it contains less than 1,5%, preferably less than 1% by weight of magnesium oxide. Preferably it contains less than 0,4% by weight of calcium oxide.

- 5 The invention also relates to products formed by the methods described herein above.

According to another aspect of the invention there is provided treated titania slag containing rutile, anatase and pseudobrookite.

According to yet another aspect of the present invention there is provided treated titania slag including rutile, anatase, ilmenite and pseudobrookite.

10 **4. Brief Description of the Drawings**

Preferred embodiments of the invention will now be described by way of example only and with reference to the accompanying drawings wherein:

Figure 1 is a X-ray diffraction pattern of as-cast titania slag;

Figure 2 is a X-ray diffraction pattern of oxidised titania slag;

- 15 **Figure 3** is a X-ray diffraction pattern of oxidised and reduced titania slag;

Figure 4 is a X-ray diffraction pattern of oxidised and reduced titania slag after leaching; and

Figure 5 is a chemical composition profile through a titania slag particle oxidised for 1 hour at 850°C in 8% oxygen.

Detailed Description of the Invention

As described above titania slag is formed by smelting ilmenite ore in an electric arc furnace to form pig iron and titania rich slag. The titania rich slag is cast in a molten state into ladles whereby solid blocks are produced ranging from a few tons to as much as forty tons. Titania slag mainly consists of a pseudobrookite solid solution phase also known as the M_3O_5 solid solution. The solid solution phase with general formula $(Fe^{2+}, Mg^{2+}, Mn^{2+}, Ti^{4+}, Ti^{3+})_3 O_5$ contains iron in the Fe(II) state, titanium in the Ti(III) and (IV) states. Potentially it can also contain iron in the Fe(III) state but then titanium in the Ti(III) state will not be present. Chemically the M_3O_5 phase contains 81 to 91% TiO_2 and between 5% and 13% FeO. The M_3O_5 phase occurs as fine to coarse grained, angular to sub-rounded greyish coloured particles with a smooth appearance. Small amounts of a silicate-rich glass can also be found, situated at the grain-and crystal boundaries of the individual M_3O_5 crystals. This glass contains a second silicate-enriched glass. The silicate-enriched glassy phase has a smooth appearance and contains finely disseminated metallic iron spheroids and droplets. The major glassy phase is fine crystalline, containing fine needle-like titanium oxide crystallites as well as fine metallic iron particles and coarser-grained "globules". The larger metallic "globules" are characterised by an iron sulphide-containing outer rim. In most instances the slag may also contain small amounts of rutile.

Table 1 shows the chemical composition of a typical titania slag that is used as feedstock to the process described in this invention. This table shows that the main impurity present in the slag is iron.

Table 1. Chemical composition of a typical titania slag, in mass percentage, used as feedstock to the process described in the current invention.

Fe ⁰	FeO	Fe ₂ O ₃	Ti ₂ O ₃	TiO ₂	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
0.21	7.65	<0.1	34.20	50.70	1.64	0.99	0.31	1.42	1.32	0.15	0.41

A typical X-ray diffraction pattern of the titania slag feedstock is presented in Figure 1. This shows: i) a main pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.52Å and a 2θ angle from 25.553° to 25.280° for Cu Kα radiation. In this specific instance rutile is present, and exhibits a main peak (r) taken at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation. In other cases rutile is not always present.

The slag is not amenable to acid leaching for removing impurities to form a TiO₂ rich upgraded slag. Accordingly the slag requires pre-treatment to render it amenable to acid leaching. The beneficiation process of titania slag accordingly includes the following steps:-

Crushing and sizing the titania slag

The blocks of titania slag are crushed and sized using conventional methods and preferably the slag is sized in the +106-850 μm particle size range which is acceptable in the chloride process for TiO₂ pigment production.

Oxidation of the sized titania slag

The crushing and sizing of the titania slag is followed by an oxidation procedure. This is conducted by reacting the sized slag at a temperature between 700°C and 950°C, preferably

between 800°C and 875°C with an oxidising atmosphere for ½ to 4 hours. A fluid bed reactor is preferred for this procedure, while the oxidising gas is preferably oxygen diluted by an inert gas (such as N₂) to levels containing between 2% and 12%O₂.

5 An optical microscopic investigation conducted on polished blocks of the oxidised samples revealed that major changes in the general appearance, as well as mineralogical composition of the as-cast slag occurred during the oxidation process. Pores formed and slag particles lost their "smooth" appearance to become zoned. Some of the larger particles had unoxidized M₃O₅ cores surrounded by a TiO₂-rich intermediate zone. Most of the smaller particles were transformed to TiO₂. The TiO₂ phases that formed were a mixture of anatase and rutile. On 10 the outside edges of all the particles were iron-enriched, slightly porous marginal zones. Figure 5 provides evidence of the iron enriched outside edge. Limited iron migration towards the edges of cracks also occurred. Inside the unoxidized M₃O₅ cores of the slag particles fine metallic iron particle, situated at the edges of fine cracks extending through the slag particles, could be observed. Most of the iron is converted to the Fe(III) state and all of the titanium is 15 present in the Ti(IV) state.

An advantage of segregation of iron towards the outer surface of the slag particles include rapid reduction roasting and ready access of the impurities to the leach solution and their rapid selective leaching.

Figure 2 shows a typical X-ray diffraction pattern for titania slag after it was subjected to the 20 oxidation procedure. This shows:

- i) a main rutile peak (r) at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;

- ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation; and
- iii) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.

5 ***Reduction of the oxidised titania slag***

The next step is to reduce the oxidised slag. This is conducted by contacting the oxidised slag particles with a reducing agent at a temperature from about 700°C to about 950°C, preferably between about 800°C and about 875°C, preferably in a fluidised bed reactor. The reduction is carried out for a period of at least 20 minutes.

- 10 The reducing agent may comprise any suitable conventional reducing agent such as carbon monoxide, hydrogen, natural gas etc, or a combination thereof. Preferably it comprises the gaseous products that result from the combustion of coal.

The general optical appearance of the slag particles after reduction is very similar to those of the oxidised products except that the iron enriched outer rims of the particles are converted to
15 ilmenite. Some of the particles can be coated with a thin layer of carbon. Most, but not all of the iron is converted to the Fe(II) state and only a very small portion of the titanium is converted to the Ti(III) state.

- A typical X-ray diffraction pattern of titania slag that was oxidised and reduced is presented in
20 Figure 3. This shows:

- i) a main rutile peak (r) at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;
- ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation;
- 5 iii) a minor ilmenite peak (i), taken at a d-spacing of 2.754Å and a 2θ angle of 32.483° for Cu Kα radiation; and
- iv) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.

Leaching of the reduced titania slag

- 10 After the oxidation and reduction roast the slag is leached in 20 wt% hydrochloric acid at the boiling point of the acid at atmospheric pressure or at elevated pressure. The solids are contacted with an excess of acid required to dissolve the iron and other impurity oxides. The time required for leaching will be dictated by the slag composition and the temperature used for the reaction. Optically, the leached residue displays a weathered appearance compared to
- 15 the oxidised as well as reduced products. The effect of leaching is most prominent along the outer margins of the slag particles as well as along cracks extending into the individual slag particles.

Table 2 gives the chemical composition of the beneficiated titania slag. This shows that most of the impurities have been removed from the slag and that it now conforms to the ideal

20 specification of the chloride process.

Table 2. The chemical composition of the beneficiated titania slag, in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
94.10	1.54	1.84	0.47	0.11	0.55	0.37	0.10	0.33

Figure 4 gives the X-ray diffraction pattern of titania slag after the oxidation, reduction and leach procedures. This shows:

- 5 i) a main rutile peak (r) taken at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;
- ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation;
- iii) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ
- 10 angle from 25.553° to 25.449° for Cu Kα radiation.

Drying of the leached titania slag

Following the leach procedure the leach liquor and titania slag are separated in a solid-liquid separation procedure before the titania slag is washed and then dried at temperatures between 100°C and 160°C. This removes most of the volatile by-products that resulted from the

15 interaction between the mineral acid and the titania slag.

After drying the beneficiated titania slag product contains more than 90% TiO₂, preferably between 93% and 97% TiO₂, less than 4% of total iron expressed as FeO and less than 1.2% of the alkaline earth impurities MgO and CaO combined. The main phases present in the

beneficiated titania slag are rutile and anatase, while physically only the outside rims of the particles are porous and the bulk of the particles are dense.

6. Examples

Example 1

- 5 Ilmenite from a beach sand deposit was subjected to electro-smelting in a direct current (DC) arc plasma furnace. The composition of the slag produced is presented in Table 3.

Table 3. Chemical composition of titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
86.20	9.18	1.42	0.82	0.33	1.46	1.15	0.14	0.46

- The slag was broken down by crushing and screened at +106 µm-850 µm. Following this the
10 slag was oxidised in a fluidised bed reactor at 850°C for 30 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of
15 the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 4.

Table 4. Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
94.80	2.60	1.22	0.72	0.06	0.73	0.62	0.09	0.73

Example 2

The same slag as in Example 1 was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidised in a fluidised bed reactor at 950°C for 120 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 950°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 5.

Table 5. Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
92.10	3.99	1.26	0.77	0.32	0.96	0.50	0.12	0.43

Example 3

Ilmenite from a beach sand deposit was smelted in a DC arc plasma furnace. The composition of the slag that was produced is presented in Table 6.

Table 6. Chemical composition of titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
69.70	24.83	3.50	0.89	0.30	1.88	1.07	0.33	0.47

The slag was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidised in a fluidised bed reactor at 850°C for 120 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 12%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 7.

Table 7. Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
90.60	6.35	2.07	0.60	0.18	0.63	0.24	0.16	0.32

Example 4

The same slag as in Example 1 was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidised in a fluidised bed reactor at 750°C for 120 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 4% . Thereafter it was reduced in the same reactor at 750°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted

slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 8.

5 **Table 8.** Composition of beneficiated titania slag in mass percentage

TiO_2	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	V_2O_5
91.70	4.17	1.31	0.84	0.09	1.05	0.89	0.11	0.46

Example 5

This example will illustrate the inertness of as-cast titania slag to the action of mineral acids.

Titania slag with the composition listed in Table 9 was crushed and sized in the range

10 +106 μm –850 μm .

Table 9. Chemical composition of titania slag in mass percentage

TiO_2	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	V_2O_5
87.7	10.04	1.47	1.16	0.13	0.93	1.57	0.13	0.45

This slag was leached in 20 wt% hydrochloric acid at a temperature of 95°C for 4 hours.

Following this the leach liquor was decanted and the solids were dried. The chemical analysis

15 of the leach residue is listed in Table 10.

Table 10 Chemical composition of leach residue in mass percentage

TiO_2	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	V_2O_5
88.40	9.08	1.26	1.08	0.10	0.98	1.56	0.11	0.44

Example 6

Ilmenite from a beach sand deposit was smelted in a DC arc plasma furnace. The composition
 5 of the slag that was produced is presented in Table 11.

Table 11. Chemical composition of titania slag in mass percentage

TiO_2	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	Cr_2O_3	V_2O_5
88.70	7.92	1.64	0.99	0.31	1.42	1.32	0.15	0.41

The slag was broken down by crushing and screened at +106 μm -850 μm . Following this the
 slag was oxidised in a fluidised bed reactor at 850°C for 3 hours in an oxidising atmosphere
 10 that resulted from the combustion of coal char in an excess of air. Thereafter it was reduced in
 the same reactor at 800°C for 30 minutes in a reducing atmosphere that resulted from the
 combustion of coal in the absence of excess air. The roasted slag was then leached in a
 pressure vessel at 140°C in 20 wt% hydrochloric acid for 2 hours. At the conclusion of the
 leach procedure the leach solution was decanted and the solids were washed and dried at
 15 150°C. The composition of the beneficiated titania slag is given in Table 12.

Table 12. Composition of beneficiated titania slag in mass percentage

TiO₂	FeO	SiO₂	Al₂O₃	CaO	MgO	MnO	Cr₂O₃	V₂O₅
94.6	1.82	2.03	0.40	0.14	0.40	0.30	0.09	0.29

It will be appreciated that many variations in detail are possible without thereby departing from the scope and spirit of the invention.

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CLAIMS

1. A method of treating titania slag to increase the leachability of impurities from the slag comprising the steps of
 - sizing the titania slag to a particle size from 75 to 850 μm ;
- 5 • oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
- 10 • reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state.
2. A method of treating titania slag to increase the leachability of impurities from the slag
- 15 comprising the steps of
 - sizing the titania slag to a particle size from 75 to 850 μm ;
 - oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700 °C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to

convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and

- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes, to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state.

3. The method of either one of claims 1 or 2 wherein the iron present in the slag concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilise in the slag when the slag is oxidised.

4. The method of any one of the preceding claims wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.

5. The method of claim 4 wherein the oxidation is carried out at a temperature from about 800°C to about 875°C.

6. The method of any one of the preceding claims wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

7. The method of any one of the preceding claims wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

8. A method of beneficiating titania slag to increase the TiO₂ content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 µm;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

9. A method of beneficiating titania slag to increase the TiO₂ content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 µm;

- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes, allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a substantial portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

10. The method of either one of claims 8 or 9 wherein the leaching is conducted under pressure in excess of atmospheric pressure.

11. The method of either one of claims 8 or 9 wherein the leaching is conducted at atmospheric pressure.

12. The method of any one of claims 8 to 11 wherein the acid used in the leaching step is heated.

13. The method of any one of claims 8 to 12 wherein the acid used in the leaching step comprises hydrochloric acid.

14. The method of any one of claims 8 to 13 which includes a caustic leaching step after the
5 acid leaching step.

15. The method of any one of claims 8 to 14 which includes a step of calcining the treated slag.

10 16. The method of claim 15 wherein the treated slag is washed and dried to remove volatile by products prior to the calcining step.

17. The method of either one of claims 15 or 16 wherein the calcined slag is subjected to a magnetic separation procedure.

15

18. The method of any one of claims 8 to 17 wherein the iron present in the slag concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilise in the slag when the slag is oxidised.

19. The method of any one of claims 8 to 18 wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.

20. The method of claim 19 wherein the oxidation is carried out at a temperature from about
5 800°C to about 875°C.

21. The method of any one of claims 8 to 20 wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

10 22. The method of any one of claims 8 to 21 wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.

23. A product when formed by a method of any one of the preceding claims.

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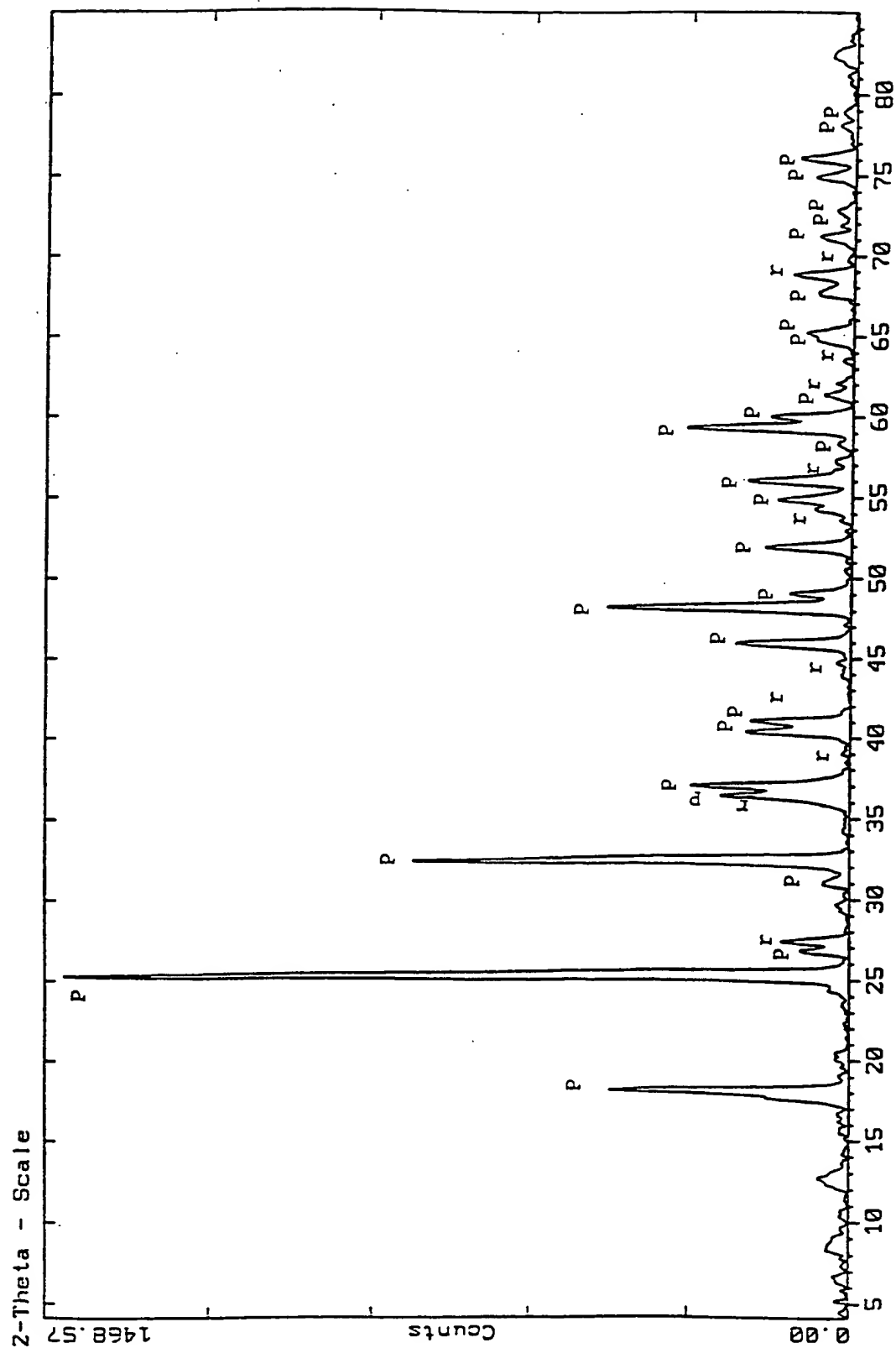


Figure 1

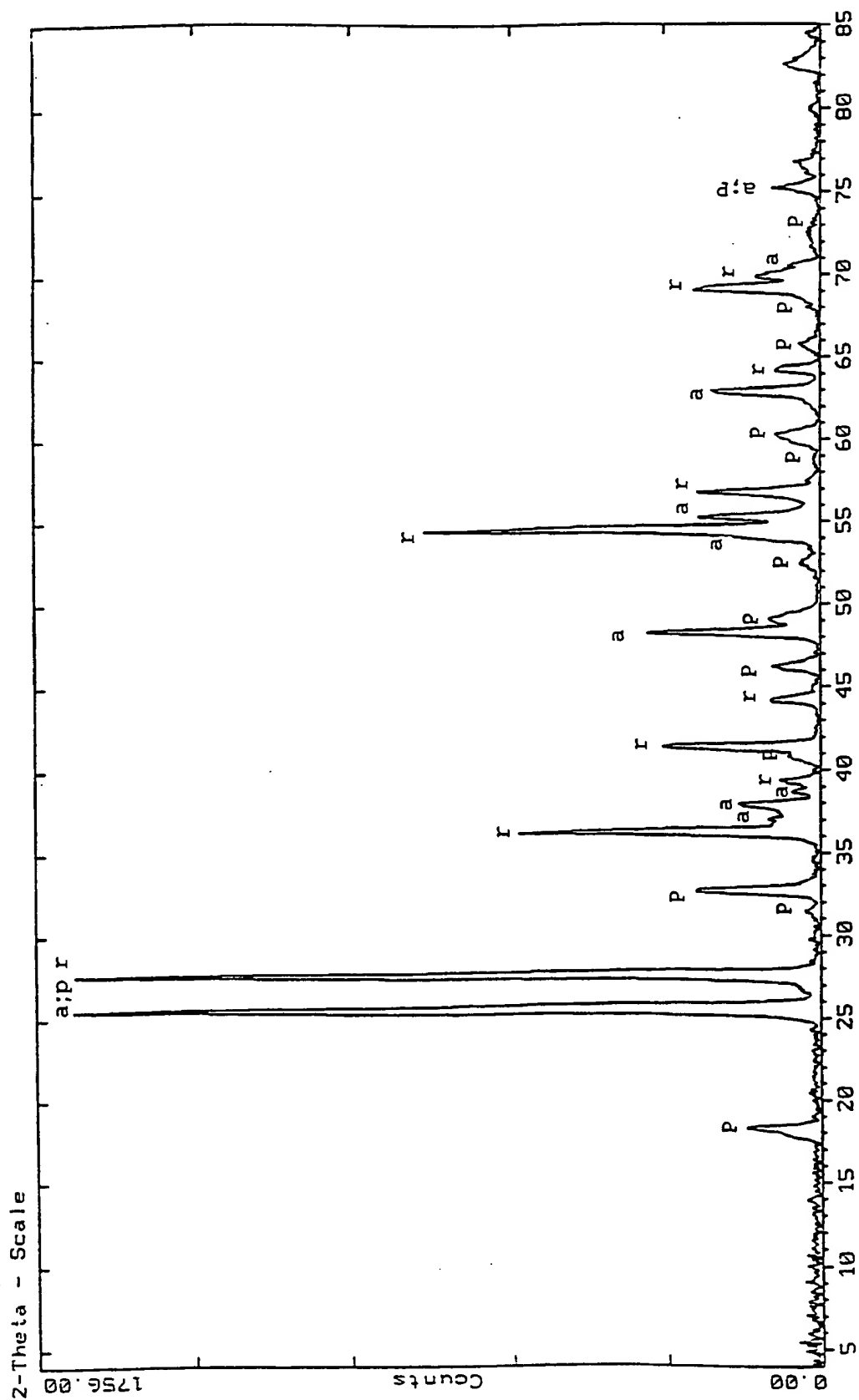


Figure 2

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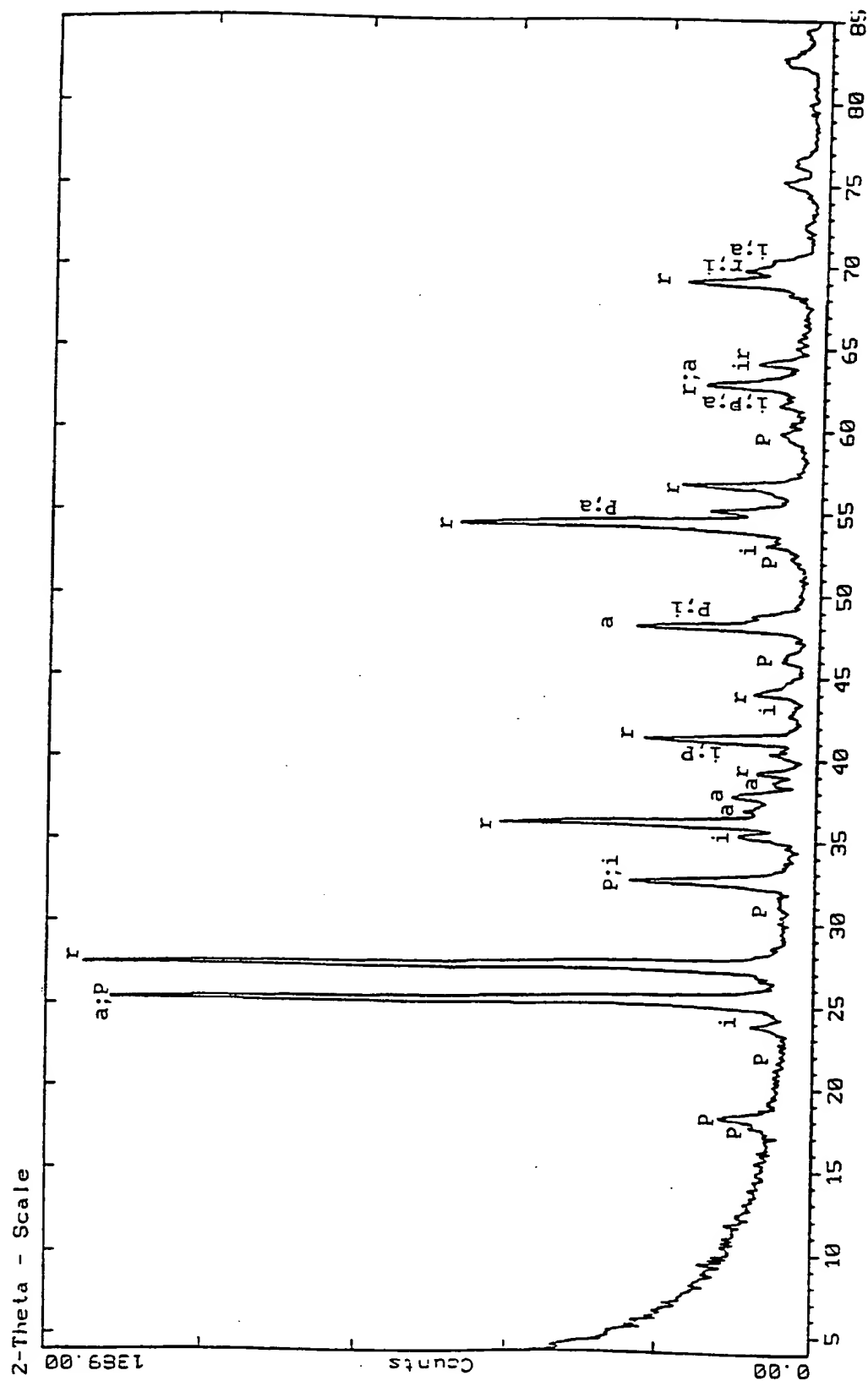


Figure 3

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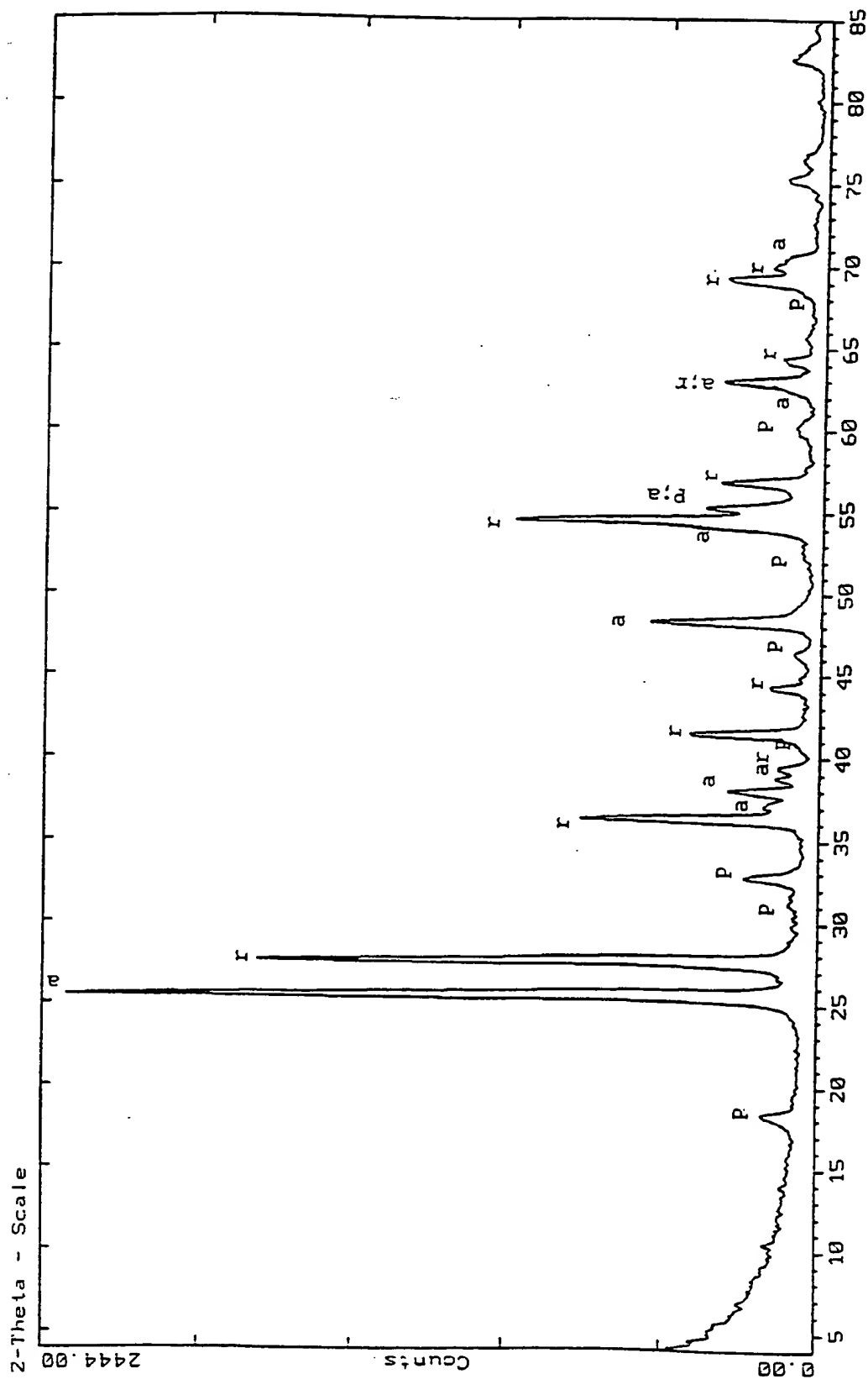


Figure 4

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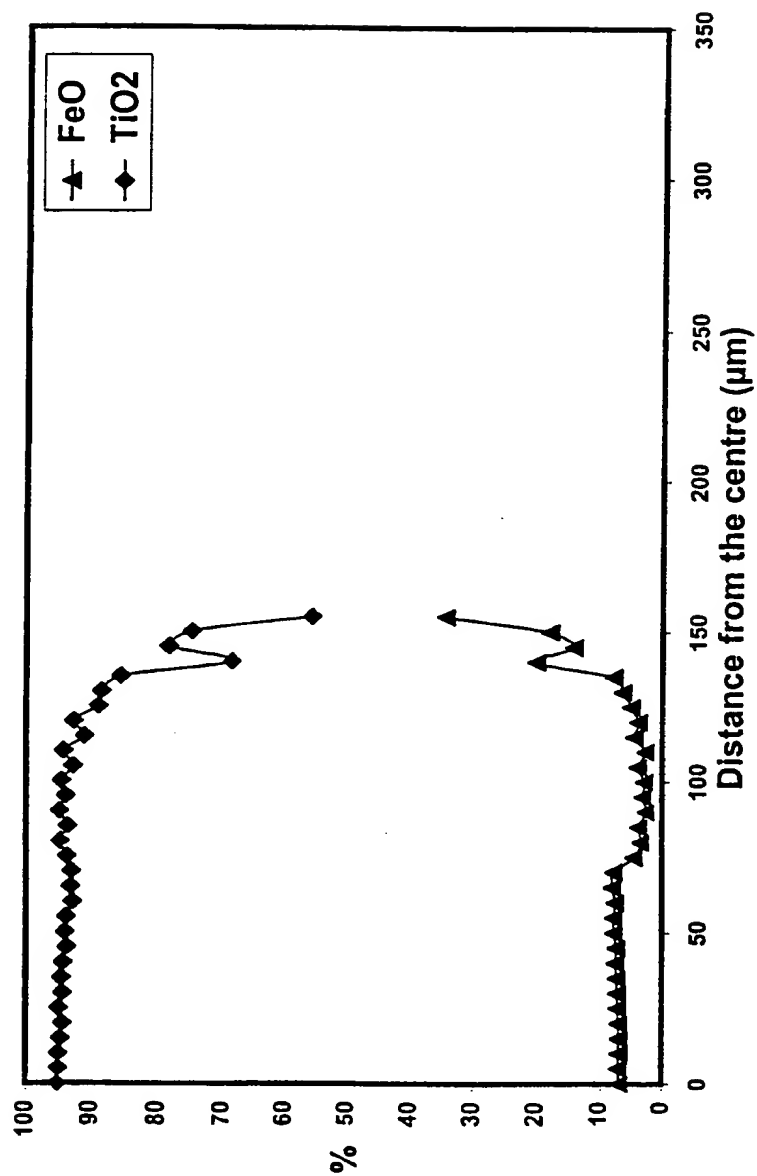


Figure 5